NASA/TM—2002-211494

Effect of Adventitious Carbon on the Environmental Degradation of SiC/BN/SiC Composites

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April 2002

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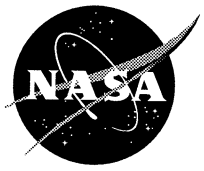

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Seventh Conference on Interphase Phenomena in Composite Materials
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Space Administration

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Abstract

Pesting remains a major obstacle to the application of SiC/SiC composites in engine service, and selective degradation of the boron nitride interphase at intermediate temperatures is of primary concern. However, significant progress has been made on interphase improvement recently, and we now know more about the phenomenon and ways to suppress it. By screening SiC/BN/SiC materials through characterization of strength and microstructures after exposure in a burner rig, some factors that control pesting in these composites have been determined. A key precaution is careful control of elemental carbon presence in the interphase region.

Introduction

SiC/SiC composites are strong contenders for high-temperature application in engine hot sections, where oxidative degradation by aggressive ambient gases makes the durability of components an important issue. In such environment the interphase (the material at the fiber-matrix interface) is key to composite behavior and component life. The interphase is designed as the weak mechanical link in a composite, to ensure debonding between fiber and matrix and deflection of cracks originating in the matrix. Unfortunately, it is also the weakest link in terms of environmental effects because the most mechanically effective interphase materials, carbon and boron nitride, are also prone to easy oxidation. Several studies in our laboratory and elsewhere have demonstrated that the highly deleterious phenomenon of pest degradation or *pesting* in SiC/SiC composites arises from selective environment attack of the interphase [1-4]. Damage from pesting ranges from generation of localized fiber flaws to embrittlement of the composite as the compliant interphase is replaced by rigid silica, which fuses the components together.

Because carbon leaves no solid residue on oxidation, it is no longer seriously considered a suitable interphase for SiC/SiC composites, and the state-of-the-art interphase in these systems is pyrolitic boron nitride. Yet *py*-BN oxidizes almost as easily as *py*-C, and the resulting oxide forms a low-melting eutectic with silica. Studies conducted from ~600 to 1000°C in a burner rig, to simulate an engine environment at intermediate temperatures, have shown that chain reactions easily set in at the fiber-matrix interface: B_2O_3 from the interphase BN dissolves the fiber and/or matrix to form a borosilicate (which may stay liquid at temperatures as low as 372°C); ambient moisture hydrolyzes the borosilicate, eventually leaving SiO_2 which bonds the fiber and matrix together.

Because carbon is a common denominator of most precursors and reaction products in the processing of SiC-based composites, it is important to understand the role it plays in the environmental degradation of these materials.

Materials and Procedure

Of the SiC/BN/SiC varieties reported in the literature only two have reached a sufficient state of development to attract serious attention for commercial or aerospace applications. Both varieties feature a matrix of melt-infiltration silicon carbide (*mi*-SiC) and chemical-vapor-infiltration boron nitride (*cvi*-BN) as the interphase. They differ in the reinforcing fibers, one utilizing the Hi-Nicalon™ or Hi-Nicalon(S)™ fibers made by Nippon Carbon Company, and the other Dow Corning's Sylramic™ fibers. Both Hi-Nicalon/BN/SiC and Sylramic/BN/SiC composites were investigated in this study under the NASA's Enabling Propulsion Materials (EPM) and Ultra-Efficient Engine Technology UEET) programs for advanced aerospace materials. They were assessed for pest resistance.

An outline of the procedure is shown in Fig. 1; details appear elsewhere [1]. Panels of the composite manufactured by Honeywell Advanced Composites Inc. (HACI), cut to expose fiber and interphase ends, were held for 100 hours in a burner rig at atmospheric pressure. The 0.3-Mach flame of the burner rig was struck by the combustion of Jet-A fuel in air and contains 10% H_2O among the combustion products. After burner rig exposure the samples were broken in tension, and characterized by Scanning Electron Microscopy (SEM) and Auger Electron Spectrometry (AES) on surfaces exposed by breaking thin slivers of the sample inside the AES spectrometer, to prevent contamination by carbon in the ambient; SEM was also performed on fracture surfaces exposed by the tensile test, and on polished surfaces. For characterization of the as-received material the SEM and AES samples were taken from the grip ends of the tensile bars (Fig. 1).

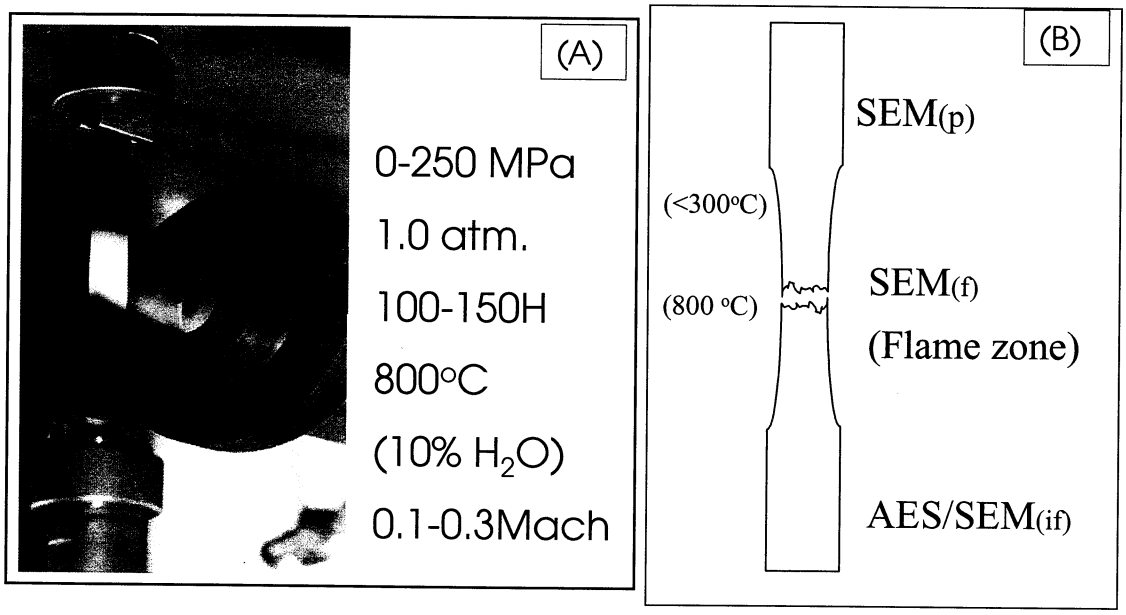

Fig. 1 (A).—Picture of burner rig exposure, and (B) schematics showing SEM and AES examination locations; sample temperatures while in the burner rig are indicated

Results and Discussion

While purity and crystallinity, as well as Si-doping, are now known to improve oxidation resistance of the BN interphase, the most significant factor in SiC/BN/SiC pesting is the occurrence of free carbon under the BN layer. In this regard, it was found that Sylramic-fiber-reinforced composites type may be further split into two categories, depending on whether polyethylene oxide (PEO) or polyvinyl alcohol (PVA) sizing was used to protect the fibers before and during composite processing. Sylramic(PVA)/BN/SiC composites showed no evidence of pesting during the 100-hour exposure in the burner rig, while the Sylramic(PEO)/BN/SiC variety pested severely. In contrast, all Hi-Nicalon/BN/SiC materials pested severely, regardless of whether the fiber was the regular Hi-Nicalon™ or Hi-Nicalon(S)™ variety. Table 1 summarizes these findings.

Sample	HN1	001	052	166	009	033	011
$\Delta\sigma$ in APBR[1]	-61%	-56%	-41%	-58%	-27%	0	0
$\Delta\varepsilon$ in APBR[1]	-90%	-78%	-80%	-75%	-28%	0	0
Fiber type	H-N[2]	HN-S[3]	HN-S[3]	Syl[4]	Syl[4]	Syl[4]	Syl[4]
Sizing type	PVA	PVA	PVA	PEO	PVA	PVA	PVA
Carbon Under BN?	yes	yes	yes	yes	no	no	no

Table 1.—Categories of SiC/BN/SiC composite determined from pest assessment ([1]From tensile test; [2] Hi-Nicalon™; [3]Hi-Nicalon(S)™; [4]Sylramic™)

The materials that exhibited severe pesting were characterized by one common feature: the presence of a continuous layer of carbon between the BN interphase and the SiC fiber. In Hi-Nicalon/BN/SiC composites the carbon was in the form of a compact film, while in the Sylramic(PEO)/BN/SiC varieties it was a skeletal network. Pesting was promoted by oxidative removal of this carbon layer, leaving the broad flank of the BN layer exposed to attack by flame oxidants. In the materials containing Hi-Nicalon-type fibers the layers of carbon came from the stoichiometric excess in the fiber; in composites made with PEO-sized Sylramic fibers, the carbon was a skeletal residue from the sizing.

Note in Fig. 1 that the flame impinged on the ends of the [0°] fibers in the horizontal tows; hence, degradation must start in these fibers. Yet pesting was determined from fracture of the [90°] fibers along the sample length. Thus, degradation spread from the [0°] to the [90°] fibers, which implies that the interphase and its associated carbon sub-layer are in contact within and between tows. That was also evident on polished sections of the samples, which showed that fiber-to-fiber contact (via the BN coating) is the rule. Clearly, contact between the BN coatings around adjacent fibers is a pre-disposing factor (without which the mere presence of a carbon layer might not cause pesting), particularly when the contact is extended to other dimensions through the splicing of tows.

Fig. 2.—SEM showing a fold of carbon around the BN interphase (magnified in inset) in a Hi-Nicalon(S)/BN/SiC composite. This material pested severely in the burner rig.

Summary and Conclusion

By exposing SiC/BN/SiC composites in the burner rig and examining them for residual strength and microstructure, it has been determined that severe pest degradation of these composites by a jet flame is associated with the presence of graphitic carbon beneath the BN. Whether it originates from excess carbon in the fiber or from desizing char yield, the carbon network undermines the interphase since its removal by oxidation creates a route for deep penetration of the composite by the ambient gases. Consequently, one important precaution in SiC/BN/SiC processing is to ensure the strict absence of elemental carbon in the interphase region.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 2002	Technical Memorandum

4. TITLE AND SUBTITLE

Effect of Adventitious Carbon on the Environmental Degradation of SiC/BN/SiC Composites

5. FUNDING NUMBERS

WU–714–04–13–00

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–13262

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—2002-211494

11. SUPPLEMENTARY NOTES

Prepared for the Seventh Conference on Interphase Phenomena in Composite Materials sponsored by the Interphase Phenomena in Composite Materials, Arcachon, France, September 9–14, 2001. L.U.J.T. Ogbuji, QSS Group, Inc., Cleveland, Ohio; H.M. Yun, Cleveland State University, Cleveland, Ohio; and J. DiCarlo, NASA Glenn Research Center. Responsible person, L.U.J.T. Ogbuji, organization code 5160, 216–433–6463.

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14. SUBJECT TERMS

SiC/SiC composites; Pest prevention and control; Elemental carbon

15. NUMBER OF PAGES

11

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	